

B. Transverse Magnetic Field

The conductivity tensors under an applied magnetic field are calculated by integrating over electronic states. The carrier distribution function, $f(\epsilon)$ is involved only in the form of $df/d\epsilon$ or $f(1-f)$ in the integrand.^{3,13} For the case of a Fermi distribution at a low temperature, the distribution function introduces into the integrand approximately a δ function, $\delta(\epsilon-\zeta)$, where ζ is the Fermi energy under the applied field. In photoconductivity where the photoexcited carriers may be considered as monoenergetic and the excitation is not too strong, we have $f \propto \delta(\epsilon_f)/\rho_f$ and $(1-f) \sim 1$ where ρ_f is the density of states at the final energy ϵ_f . Thus we may expect that approximately

$$\Delta\sigma_{xx} \propto \sigma_{xx}^F(\epsilon_f)/\rho_f, \quad (14)$$

$$\Delta\sigma_{zz} \propto \sigma_{zz}^F(\epsilon_f)/\rho_f, \quad (15)$$

where $\sigma^F(\epsilon_f)$ is the conductivity of degenerate carriers with the Fermi energy equal to ϵ_f . The quantity ρ_f exhibits a maximum whenever ϵ coincides with a Landau level. At high magnetic fields, σ_{zz}^F gives minima whereas σ_{xx}^F gives maxima near Landau levels, therefore, ρ_f enhances the oscillation of photoconductivity

¹³ S. S. Shalyt and A. L. Efros, *Fiz. Tverd. Tela* **5**, 1233 (1962) [English transl.: *Soviet Phys.—Solid State* **4**, 903 (1962)].

in a longitudinal field and counteracts the effect of σ_{xx}^F for the oscillation in a transverse field. This is consistent with the fact that oscillations observed in transverse fields were less pronounced than those observed in longitudinal fields and that sometimes the additional structure appeared even reversed as indicated by Fig. 5.

The above consideration applies to high magnetic fields with $\omega_c\tau \gg 1$. In a weak field with $\omega_c\tau \lesssim 1$, the maxima of σ_{xx}^F near Landau levels involve the lateral drift motion due to scattering among quantized orbits and are more uncertain than the minima in σ_{zz}^F which are mainly the effect of the distribution of electronic states on scattering. This situation can be seen in the results of de Haas-Schubnikov effect measurements on *n*-type GaSb.¹⁴ With $\omega_c\tau \lesssim 2$, the ratio of observed oscillation amplitudes of transverse and longitudinal magnetoresistances was smaller than expected from the theory for $\omega_c\tau \gg 1$. It would be desirable to extend the photoconductivity measurements to higher magnetic fields but it should be borne in mind that only Landau levels within $\hbar\omega_0$ of the band edge produce structures in the spectrum.

¹⁴ W. M. Becker and H. Y. Fan, in *Proceedings of the Seventh International Conference on the Physics of Semiconductors, Paris, 1964* (Dunod Cie., Paris, 1964), p. 663; T. O. Yep and W. M. Becker, *Phys. Rev.* **144**, 741 (1966).

Statistical Theory of Localized States of a Many-Impurity Crystal*

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A statistical theory of energy levels and position probability is derived for a one-dimensional, statistically dilute, many-impurity crystal. The equations are evaluated for a simple model. It is shown that two impurity bands are generated, one above and one below the host band, each merging without a gap onto the host band. If U is greater than (less than) zero, the upper (lower) band is more dense. Each impurity-level electron is shown to be distributed in a wavelike manner along the impurities. The equations are derived for impurities differing both in their self-energy and in their nearest-neighbor coupling from the host monomers.

I. INTRODUCTION

IT is well known that impurities in crystals result in the appearance of so-called localized "impurity states," separated from the main band by a gap. The conditions for the appearance of such localized states and their location can be determined by the Green's-function method of Koster and Slater.¹⁻³ A very similar situation occurs for excited states in molecular crystals, where impurities again generate, under specified condi-

tions, localized levels in the neighborhood of an exciton band.^{4,5} Lifshitz⁶ considers a disordered system, i.e., a nonregular impurity distribution, and calculates the spectral density by expanding in powers of the impurity concentration.

In his theory there is only one parameter which describes the impurity distribution, namely, the mean distance between impurities, related inversely to their concentration. Impurity-impurity coupling is taken into account, but only as a small perturbation on an infinitely dilute system.

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¹ G. F. Koster and J. C. Slater, *Phys. Rev.* **95**, 1167 (1954).

² G. F. Koster, *Phys. Rev.* **95**, 1436 (1954).

³ G. F. Koster and J. C. Slater, *Phys. Rev.* **96**, 1208 (1954).

⁴ R. E. Merrifield, *J. Chem. Phys.* **38**, 920 (1963).

⁵ S. Takeno, *J. Chem. Phys.* **44**, 853 (1966).

⁶ I. M. Lifshitz, *Advan. Phys.* **3**, 483 (1964).

II. DERIVATION OF MANY-IMPURITY BAND

In this paper we take a somewhat different approach from Lifshitz. The basic equation of the Koster-Slater method¹ for a many-impurity problem with no interband mixing is

$$\chi(p) - \sum_j \chi(j) \sum_i V(i, j) G_{pi} = 0, \quad (1)$$

where $\chi(p)$, $\chi(j)$ are the coefficients of the Wannier amplitudes at the p th and the j th site occupied by an impurity. $V(i, j)$, the impurity matrix element connecting site i and j of the lattice and G_{pi} , is the Green's function connecting these sites:

$$G_{pi} = \frac{1}{2\pi} \int_{-\pi}^{\pi} \frac{dk}{E - \epsilon(k)} e^{ik(n_p - n_i)}. \quad (2)$$

Here E is the desired energy, $\epsilon(k)$ the energy levels of a band of the unperturbed Hamiltonian, and n_p , n_i measure the distance between the p th and the i th elementary cell in units of a , the cell dimension. We now assume (a) a one-dimensional crystal; (b) $V(i, j) = \delta_{ij}U$; (c) many $(2m-1)$ impurities, where (d) the average distance between two impurities, $L_0 = n_0 a$ obeys $n_0 \gg 1$. We simplify the notation to

$$y = 1 - UG_0, \\ y_{ij} = UG_{ij},$$

and hence the equation yielding the impurity energy levels for a particular impurity distribution is

$$\begin{vmatrix} y & -y_{12} & -y_{13} & \cdots & -y_{12m-1} \\ -y_{12} & y & -y_{23} & \cdots & \\ & & & \ddots & \\ & & & & y \end{vmatrix} = 0. \quad (3)$$

But our two assumptions (d) and (e) justify truncating the Green's-function sequence after the nearest-neighbor impurity term—i.e., we only include those Green's functions which couple a given impurity to its nearest impurity on either side. In Eq. (3) we therefore neglect all y_{ij} except y_{i+1} , y_{i-1} ; this equation reduces therefore to the following:

$$\Delta_{2m-1} = \begin{vmatrix} y & -y_{12} & 0 & 0 & 0 & \cdots & 0 \\ -y_{12} & y & -y_{23} & 0 & 0 & \cdots & 0 \\ 0 & -y_{23} & y & -y_{34} & 0 & \cdots & 0 \\ & 0 & & & \ddots & & \\ & & & & & & y \end{vmatrix} = 0. \quad (4)$$

This determinant can be expanded in powers of y , resulting in the following equation:

$$y^{2m-1} + \sum_{p=1}^{m-1} y^{2m-2p-1} (-1)^p B_p(2m-1) = 0, \quad (5)$$

where the coefficients $B_p(2m-1)$ are

$$B_p(2m-1) = \sum_{\substack{r_1 r_2 \cdots r_p = 1 \\ r_1 \neq r_2, r_2 \neq r_3, r_3 \neq r_4, \dots \\ \neq \cdots \neq r_p, r_p \neq 1}} y_{r_1, r_1+1}^2 y_{r_2, r_2+1}^2 \cdots y_{r_p, r_p+1}^2. \quad (6)$$

For proof, see Appendix A. Now examine B_p more closely. It is a sum of $N_p(2m-1)$ terms, where each term is a product of p factors. Each of these factors has the form

$$y_{r_1, r_1+1}^2 = \left(\frac{U}{2\pi} \right)^2 \int_{-\pi}^{\pi} \frac{dk}{E - \epsilon(k)} \int_{-\pi}^{\pi} \frac{dk'}{E - \epsilon(k')} \\ \times \exp[i(k-k')(n_{r_1} - n_{r_1+1})], \quad (7)$$

i.e., it differs from the other factors only in the number $n_r - n_{r+1}$, representing the distance between two adjacent impurities. Hence, each term can be uniquely characterized by the set of p lengths occurring in it.

Let $P(n)$ be the probability that two adjacent impurities are separated a distance na . Then, if $N_p(2m-1)$ is large, it follows that a particular term, characterized by the set n_1, n_2, \dots, n_p will occur in B_p approximately $N_p(2m-1)P(n_1)P(n_2)\cdots P(n_p)$ times. Hence, also, the sum over r_1, r_2, \dots, r_p can be replaced by a sum over n_1, n_2, \dots, n_p , i.e.,

$$B_p(2m-1) \approx \left(\frac{U}{2\pi} \right)^{2p} \\ \times \sum_{n_1, \dots, n_p=1}^{N_0} N(p, 2m-1) P(n_1) P(n_2) \cdots P(n_p) \\ \times \int_{-\pi}^{\pi} \frac{dk_1}{E - \epsilon(k_1)} \int_{-\pi}^{\pi} \frac{dk'}{E - \epsilon(k')} e^{in_1(k_1 - k')} \\ \times \cdots \int_{-\pi}^{\pi} \frac{dk_p}{E - \epsilon(k_p)} \int_{-\pi}^{\pi} \frac{dk'}{E - \epsilon(k')} e^{in_p(k_p - k')}, \quad (8)$$

or

$$B_p(2m-1) = (U/2\pi)^{2p} N(p, 2m-1) F^p(E), \quad (9)$$

where

$$F(E) = \int_{-\pi}^{\pi} \frac{dk}{E - \epsilon(k)} \int_{-\pi}^{\pi} \frac{dk'}{E - \epsilon(k')} \sum_{n=1}^{N_0} P(n) e^{in(k-k')}. \quad (10)$$

Now consider the following simpler problem. Suppose that all impurities were equally spaced, so that $y_{12} = y_{23} = y_{34} = Q$. Then, by Eq. (6),

$$B_p(2m-1) = N(p, 2m-1) Q^{2p}.$$

Our problem is therefore now mathematically identical

to the problem of equally spaced impurities, where $(U/2\pi)^2 F = Q^2$. But this latter problem can be trivially solved. It has the solution

$$y = 2Q \cos(r\pi/2m), \quad (11)$$

or

$$y^2 = 4Q^2 \cos^2(r\pi/2m), \quad r = 1, 2, \dots, m-1.$$

In terms of our analogy,

$$y^2 = \frac{U^2 F}{\pi^2} \cos^2 \frac{r\pi}{2m}, \quad r = 1, 2, \dots, m-1 \quad (12a)$$

or, equivalently,

$$y^2 = \frac{U^2 F}{\pi^2} \sin^2 \frac{r\pi}{2m}, \quad r = 1, 2, \dots, m-1. \quad (12b)$$

This same solution can also be generated by finding $N(p, 2m-1)$ and then summing Eq. (5). We present this method in Appendix B.

In light of the above we can now extend the theory somewhat by assuming that the impurity differs from the host not only in the diagonal matrix element of the Hamiltonian, U , but also in the coupling of the impurity to its nearest neighbors, i.e., to its adjacent host monomers. We then relabel:

$$V(i, j) = \delta_{ij} U_1 + U_2 (\delta_{i, j+1} + \delta_{i, j-1}). \quad (13)$$

Equation (1) then becomes

$$\chi(p) - \sum_j \chi(j) \{ U_1 G_{pj} + U_2 [G_{pj+1} + G_{pj-1}] \} = 0. \quad (14)$$

We keep all other assumptions, and hence again truncate the Green's functions by keeping only nearest-neighbor impurity-impurity interactions. Define now

$$G_{pj+1} + G_{pj-1} = G_{pj}^0 \quad (15)$$

so that we have simply replaced UG_{ij} in the previous problem by $U_1 G_{ij} + U_2 G_{ij}^0$. Since the dependence of this new term on interimpurity distance is the same as before, the arguments of the simpler case go through exactly as before. We can therefore conclude that for this two-parameter impurity crystal the impurity band is determined by the equation

$$[1 - U_1 G(0) - U_2 G^0(0)]^2 = (1/\pi^2) F_1(E) \cos^2(r\pi/2M), \quad (16)$$

where

$$F_1(E) = \sum_{n=1}^{N_0} P(n) \left[U_1 \int \frac{dk}{E - \epsilon(k)} e^{ikn} + 2U_2 \int \frac{dk}{E - \epsilon(k)} e^{ikn} \cos k \right]^2, \quad (17)$$

$$\begin{aligned} F_1(E) = & U_1^2 \int_{-\pi}^{\pi} \frac{dk}{E - \epsilon(k)} \int_{-\pi}^{\pi} \frac{dk'}{E - \epsilon(k')} \sum_{n=1}^N P(n) e^{in(k-k')} \\ & + 4U_2^2 \int_{-\pi}^{\pi} \frac{dk}{E - \epsilon(k)} \int_{-\pi}^{\pi} \frac{dk'}{E - \epsilon(k')} \cos k \cos k' \\ & \times \sum_{n=1}^N P(n) e^{in(k-k')} + 4U_1 U_2 \int_{-\pi}^{\pi} \frac{dk}{E - \epsilon(k)} \\ & \times \int_{-\pi}^{\pi} \frac{dk'}{E - \epsilon(k')} \cos k' \sum_{n=1}^N P(n) e^{in(k-k')}. \quad (18) \end{aligned}$$

The energy levels can now be found, using either Eq. (12b) or Eq. (16), by graphical or numerical means. At this point we shall simply investigate the question whether the impurity levels found are separated by a gap from the main host band. To do so we assume that $\epsilon(k^*)$ represents either the top or bottom of the host band, set $E = \epsilon(k^*) + \eta$, with $\eta \rightarrow 0$. We then find, using either Eqs. (12b) or (16), the condition

$$\sin^2(r\pi/2M) = \frac{1}{4},$$

which holds for $r = \frac{1}{2}M$. We therefore find no gap—i.e., the impurity levels merge directly onto the host band.

III. DERIVATION OF AN AVERAGE IMPURITY LOCALIZATION PROBABILITY

Since impurities frequently serve as traps, it is of interest to know the probability of finding the electron (or the exciton) on a given impurity. In our case we write down this localization probability for a particular impurity distribution and then form the average according to the assumed statistical distribution function.

To be concrete: Going back to Eq. (1) and making the stated approximations leads to

$$\begin{aligned} yX_1 - y_{12}X_2 &= 0, \\ -y_{kk-1}X_{k-1} + yX_k - y_{kk+1}X_{k+1} &= 0, \\ k &= 2, 3, \dots, 2m-2 \quad (19) \\ -y_{2m-1, 2m-2}X_{2m-2} + yX_{2m-1} &= 0. \end{aligned}$$

This set of equations can be solved for the X 's. It can be shown, for example by induction, that these coefficients are given by

$$\begin{aligned} X_{2k} &= X_1 [y_{12}y_{23} \dots y_{2k-1, 2k}]^{-1} \\ &\times \sum_{p=0}^{k-1} y^{2k-2p-1} (-1)^p B_p(2k-1), \\ X_{2k-1} &= X_1 [y_{12}y_{23} \dots y_{2k-2, 2k-1}]^{-1} \\ &\times \sum_{p=0}^{k-1} y^{2(k-p-1)} (-1)^p B_p(2k-2). \quad (20) \end{aligned}$$

Now form $|\chi_{2k}/\chi_1|^2$. It has the form

$$|\chi_{2k}/\chi_1|^2 = \sum_{p,q=0}^{k-1} (-1)^{p+q} (y)^{4k-2p-2q-2} J_{pq}, \quad (21)$$

where $J_{pq} = D_{kp} H_{kq}$ with

$$D_{kp} = B_p(2k-1) \left(\prod_{l=1}^{2m-2} y^{2l} \right)^{-1} \quad (22)$$

and

$$H_{kq} = B_q(2k-1) \left(\prod_{l=2k}^{2m-2} y^{2l} \right). \quad (23)$$

Now, $B_p(2k-1)$ is a sum of terms, with each term being contained in

$$\prod_{l=1}^{2m-2} y^{2l} l+1;$$

i.e.,

$$D_{kp} = \sum_{r_1 \dots r_p=1}^{2k-2} \left(\prod_{\substack{l=1 \\ l \neq r_1, r_2, \dots, r_p}}^{2m-2} y^{2l} l+1 \right)^{-1}. \quad (24)$$

Each of these terms in the sum of Eq. (24) consists of $(2m-2-p)$ factors; since p has a maximum of $k-1$, and k has a maximum of m , we have at least m factors in each term. We can therefore assume that these terms will contain interimpurity distances in accordance to the statistical distribution, i.e.,

$$S_p = \prod_{\substack{l=1 \\ l \neq r_1, r_2, \dots, r_p}}^{2m-2} y^{2l} l+1 = y^{2(n_1)P(n_1)(2m-2-p)} \times y^{2(n_2)P(n_2)(2m-2-p)} \dots y^{2(n_x)P(n_x)(2m-2-p)} \dots$$

Hence

$$\begin{aligned} \ln S_p &= \sum_j \ln [y^{2(n_j)}]^{P(n_j)(2m-2-p)} \\ &= (2m-2-p) \sum_j P(n_j) \ln y^{2(n_j)}, \end{aligned} \quad (25)$$

which leads to

$$S_p = G^{(2m-2-p)} = \exp \left\{ (2m-2-p) \int_0^\infty P(n) \ln y^2(n) dn \right\}.$$

Thus

$$D_{kp} = N(p, 2k-1) G^{2m-2-p}. \quad (26)$$

Now consider H_{kq} which consists of terms each of which contains $q+2m-2k-1$ factors: Since q could be 1, we must restrict $2k$ to run between 1 and m if we wish to guarantee good statistics. But such a restriction is not serious since we clearly can assume $|\chi_{2k}/\chi_1|^2$ to be symmetric about $k=m$ on the average. It follows then that

$$H_{kq} = N(q, 2k-1) G^{2m-1-2k+q}. \quad (27)$$

We find from (21) that $|\chi_{2k}/\chi_1|^2$ is

$$\begin{aligned} |\chi_{2k}/\chi_1|^2 &= \sum_{q,p=0}^{k-1} (-1)^{p+q} y^{4k-2p-2q-2} G^{p+q-(2k-1)} \\ &\quad \times N(p, 2k-1) N(q, 2k-1) \\ &= \left(\frac{G}{y^2} \right)^2 \left[\sum_{p=0}^{k-1} (-1)^p (y^2/G)^{k-p} \binom{2k-1-p}{2k-1-2p} \right]^2, \end{aligned} \quad (28)$$

where we have used Appendix B for the value of $N(p, 2k-1)$. This sum can be represented as a hypergeometric series, which in turn is of a standard type, i.e.,

$$\begin{aligned} &\sum_{p=0}^{k-1} (-1)^p (y^2/G)^{k-p} \binom{2k-1-p}{2k-1-2p} \\ &= \sum_{s=1}^k (-1)^{s+k} (y^2/G)^s \binom{k+s-1}{2s-1} \\ &= k(-1)^{k+1} (y^2/G)_2 F_1 [k+1, -k+1; \frac{3}{2}; y^2/4G] \\ &= (-1)^{q+1} (y^2/G) \frac{\sin 2kz}{\sin 2z}, \end{aligned} \quad (29)$$

where

$$\sin^2 z = y^2/4G. \quad (30)$$

Hence

$$\left| \frac{\chi_{2k}}{\chi_1} \right|^2 = \frac{\sin^2 2kz}{\cos^2 z}. \quad (31)$$

Using the same procedure we can also evaluate $|\chi_{2k-1}/\chi_1|^2$; we find

$$\left| \frac{\chi_{2k-1}}{\chi_1} \right|^2 = \frac{\cos^2(2k-1)z}{\cos^2 z}. \quad (32)$$

By (12b),

$$\sin^2 z = \frac{u^2 F}{4\pi^2 G} \sin^2 \frac{r\pi}{2M}. \quad (33)$$

So, given a particular statistical energy level we can calculate the localization probability corresponding to that level.

As can be seen from Eqs. (31) and (32), the electrons are localized in a wave-like manner along the impurities. To determine the absolute magnitude of this localization, we must normalize these probabilities. This can be done as follows.

Let Latin symbols i, j, \dots represent impurity sites, and let Greek symbols α, \dots represent host sites. According to (1),

$$\chi(j) = U \sum_i \chi(i) G_{ij}, \quad (34)$$

$$\chi(\alpha) = U \sum_i \chi(i) G_{i\alpha}.$$

Hence

$$\sum_{\alpha} \chi^2(\alpha) + \sum_j \chi^2(j) = 1 = U^2 \sum_{i,m} \chi(i) \chi^*(m) \times [\sum_{\alpha} G_{i\alpha} G_{m\alpha} + \sum_j G_{ij} G_{mj}]. \quad (35)$$

But the final two sums over α and j simply yield a sum over *all* N_0 crystal sites: The expression in brackets therefore becomes

$$\begin{aligned} \sum_{r=1}^{N_0} G_{ir} G_{mr} &= \frac{1}{N_0^2} \sum_{kk'} \frac{1}{[E - \epsilon(k)][E - \epsilon(k')]} \\ &\times \sum_{r=1}^{N_0} e^{ik(R_i - R_r)} e^{-ik'(R_m - R_r)} \\ &= \frac{1}{N_0^2} \sum_{kk'} \frac{e^{i(kR_i - k'R_m)}}{[E - \epsilon(k)][E - \epsilon(k')]} \sum_{r=1}^{N_0} e^{iR_r(k - k')}. \end{aligned} \quad (36)$$

But the final sum is $N_0 \delta_{kk'}$. Hence

$$\sum_{r=1}^{N_0} G_{ir} G_{mr} = \frac{1}{N_0} \sum_k \frac{e^{i(kR_i - R_m)}}{[E - \epsilon(k)]^2}.$$

We therefore find

$$1 = \frac{U^2}{2\pi} \sum_{i,m} \chi(i) \chi^*(m) \int_{-\pi}^{\pi} \frac{e^{ix(i-m)} dx}{[E - \epsilon(x)]^2}. \quad (37)$$

We now make the nearest-neighbor Green's-function truncation, i.e., we keep, for fixed m , $i = m, m \pm 1$. Hence

$$\begin{aligned} 1 &= \frac{U^2}{2\pi} \left\{ \int_{-\pi}^{\pi} \frac{dx}{[E - \epsilon(x)]^2} \sum_m \chi^2(m) + \int_{-\pi}^{\pi} \frac{\cos x dx}{[E - \epsilon(x)]^2} \right. \\ &\quad \left. \times \sum_m \chi^*(m) [\chi(m+1) + \chi(m-1)] \right\}. \end{aligned} \quad (38)$$

The final sum causes difficulty. To evaluate it we remember that

$$y\chi(m) = y_{mm+1}\chi(m+1) + y_{mm-1}\chi(m-1)$$

and replace y_{mm+1} , y_{mm-1} by the corresponding average y , i.e.,

$$y(n_0) = \frac{U}{2\pi} \int_{-\pi}^{\pi} \frac{e^{in_0 x} dx}{E - \epsilon(x)}.$$

We thus get as an approximate normalization condition

$$\begin{aligned} \sum_m \chi^2(m) &= \left[\frac{U^2}{2\pi} \int_{-\pi}^{\pi} \frac{dx}{[E - \epsilon(x)]^2} \right. \\ &\quad \left. + \frac{y}{y(n_0)} \frac{U^2}{2\pi} \int_{-\pi}^{\pi} \frac{\cos x dx}{[E - \epsilon(x)]^2} \right]^{-1}. \end{aligned} \quad (39)$$

It is important to note that this right-hand-side expression does not depend on the number of lattice sites N_0 , but on the strength of the impurity and the energy of the state.

These expressions can be immediately generalized for the case where the impurity-host nearest-neighbor coupling differs from that of the host monomers. The expression $\ln[y^2(n)]$ in G is replaced by

$$\ln \left[\int_{-\pi}^{\pi} \frac{kd}{E - \epsilon(k)} e^{ikn} (U_1 + 2U_2 \cos k) \right]^2 \quad (40)$$

and y^2 in Eq. (30) is replaced by $[1 - U_1 G(0) - U_2 G^0(0)]^2$. Equation (33) then becomes

$$\sin^2 z' = \frac{U^2 F_1(E)}{4\pi^2 G^1} \sin^2 \frac{r\pi}{2m}, \quad (41)$$

where

$$G^1 = \exp \int P(n)$$

$$\times \ln \left[\int_{-\pi}^{\pi} \frac{dk}{E - \epsilon(k)} e^{ikn} (U_1 + 2U_2 \cos k) \right]^2, \quad (42)$$

and F_1 is defined by Eq. (17).

IV. MODEL CALCULATION

We now test the theory for the simple case where $\epsilon(k) = \epsilon_0 + \epsilon_1 \cos k$, and we assume that the impurity differs from the host only in the self energy, i.e., in one parameter U .

For this case y can be immediately found by contour integration:

$$y = 1 \mp \lambda / (\beta^2 - 1)^{1/2}, \quad (43)$$

where $\lambda \equiv U/\epsilon_1$, $\beta = (E - \epsilon_0)/\epsilon_1$, the upper $(-)$ sign holds for $\beta > 0$, and the lower $(+)$ sign for $\beta < 0$.

To calculate $F(E)$, first calculate

$$H(E) = \left| \int_{-\pi}^{\pi} \frac{dk}{E - \epsilon(k)} e^{ikn} \right|^2. \quad (44)$$

Using contour integration we find

$$H(E) = \frac{4\pi^2 [(\beta^2 - 1)^{1/2} - |\beta|]^{2n}}{\epsilon_1^2 \beta^2 - 1}. \quad (45)$$

To proceed we must settle on a distribution function; choose a normal distribution with a mean distance n_0 between two adjacent impurities and a standard deviation σ about n_0 , with $\sigma \ll n_0$, i.e.,

$$P(n) = A e^{-(n - n_0)^2 / 2\sigma^2}, \quad (46)$$

where we normalize $\int_0^\infty P(n) dn$ to 1 and hence find

$$A = \frac{2}{\sigma\pi} \left(1 + \operatorname{erf} \frac{n_0}{\sqrt{2}\sigma} \right)^{-1}. \quad (47)$$

Since by assumption $n_0/\sqrt{2}\sigma \gg 1$, $A \approx (2\pi\sigma)^{-1/2}$. Now

$$F(E) = \frac{4\pi^2}{\epsilon_1^2 (\beta^2 - 1)} \int_0^\infty P(n) e^{n \ln Q} dn, \quad (48)$$

where

$$Q \equiv [(\beta^2 - 1)^{1/2} - |\beta|]^2.$$

Using Eq. (46), (48) becomes

$$F(E) = \frac{4\pi^2}{\epsilon_1^2 (\beta^2 - 1)} \frac{Q^{n_0}}{1 + \operatorname{erf}(n_0/\sqrt{2}\sigma)} e^{\frac{1}{2}\sigma \ln^2 Q} \times \begin{cases} 1 + \operatorname{erf}(\gamma/\sqrt{2}\sigma), & \gamma > 0 \\ 1 - \operatorname{erf}(|\gamma|/\sqrt{2}\sigma), & \gamma < 0 \end{cases} \quad (49)$$

where

$$\gamma = n_0 + \sigma \ln Q.$$

These expressions for y and F can now be used in Eq. (12b). An inspection of the resultant graphs evinces the following qualitative features:

- (1) For all σ and for all U , two impurity bands arise, one above and one below the main band.
- (2) The density of levels in these impurity bands is in the ratio of 2 to 1, independent of σ , where, for $U > 0$, the upper band is favored and for $U < 0$, the lower band is favored.
- (3) The two impurity bands join smoothly onto the main band—i.e., there is no gap. The net effect therefore is to broaden the original band by adding localized levels to its top and bottom.

We can similarly evaluate G^1 from Eq. (42). It can be shown by a straightforward calculation that

$$G^1 = [\lambda^2/(\beta^2 - 1)] Q^{n_0} (Q)^u, \quad (50)$$

where

$$u \equiv \frac{(2\sigma/\pi)^{1/2} e^{-n_0^2/2\sigma}}{1 + \operatorname{erf}(n_0/(2\sigma)^{1/2})} \approx 0. \quad (51)$$

It follows from Eqs. (49) and (51) that

$$\frac{U^2 F}{4\pi^2 G^1} \cong e^{\frac{1}{2}\sigma \ln^2 Q} \left(\frac{1 \pm (\operatorname{erf}(|\gamma|/(2\sigma)^{1/2}))}{2} \right),$$

so that, for that special case $\sigma = 0$,

$$\left| \frac{\chi_{2k-1}}{\chi_1} \right| = \left(\cos \frac{r\pi}{2m} \right)^{-2} \cos^2 \frac{(2k-1)r\pi}{2m}, \quad (52)$$

$$\left| \frac{\chi_{2k}}{\chi_1} \right|^2 = \left(\cos \frac{r\pi}{2m} \right)^{-2} \sin^2 \frac{rk\pi}{m}.$$

V. CONCLUSION

We have derived for a one-dimensional crystal, containing many identical impurities which are distributed statistically with a mean distance n_0 between adjacent impurities much larger than the elementary cell length,

expressions for (a) the energy and (b) the localization probabilities on the impurities. This is done for both the case where the impurity differs only in the self-energy and also where it differs in its nearest-neighbor coupling.

The energy levels are shown to merge onto the host band and are explicitly calculated for a model case. It is shown there that for $U > 0$, two impurity bands are generated, a denser one at the top, and the less dense one at the bottom. For $U < 0$ the situation is reversed. The localization probabilities on the impurities are similarly calculated and are shown to be distributed along the impurities like a sinusoidal wave. These electrons are therefore *delocalized* on the impurities.

Whether this theory can be extended to two- or three-dimensional crystals or to include interband coupling is not clear yet. It should be applicable to one-dimensional macromolecules, like DNA, with widely spaced bands.

APPENDIX A

It follows, simply by expansion of Δ_L , that any determinant of the form of Eq. (4) obeys

$$\Delta_L = y\Delta_{L-1} - y_{L1}L \dots L^2 \Delta_{L-2}.$$

To prove Eq. (6), start with the first few terms, e.g.,

$$\Delta_0 = 1, \quad (\Delta_{-1} = 0)$$

$$\Delta_1 = y,$$

$$\Delta_2 = y^2 - y_{12}^2,$$

$$\Delta_3 = y^3 - y(y_{12}^2 + y_{32}^2),$$

and then prove by induction. This latter also requires the assumed form for Δ_{2k} :

$$\Delta_{2k} = y^{2k} + \sum_{p=1}^k y^{2k-2p} (-1)^p B_p(2k).$$

APPENDIX B

Consider first $N(p, 2m)$. This number is identical to the number of different ways of taking p adjacent, non-overlapping pairs of integers out of the set of integers 1 to $2m$. Let us work with holes (i.e., integers *not* removed). Suppose $p = m - 1$, i.e., in each term of $B_{m-1}(2m)$ only one pair is missing. Hence in the set 1 to $2m$ we have two holes. The lowest hole must be odd, for otherwise there is a lower hole, the upper hole must be even, otherwise there is another hole which is even higher. Now proceed to count. If the first hole is 1 the second hole can be 2, 4, $2m$, i.e., there are m different sets. Proceed now to 3, 5... up to $2m - 1$ and get the following table:

1st hole:	No. of possible sets:
1	m
3	$m - 1$
\vdots	
$2m - 1$	1
$N(m - 1, 2m) =$	$\frac{1}{2}m(m + 1).$

Now let $p = m - 2$, i.e., remove two pairs, of four integers. The lowest hole must be odd, the next even, the next odd, and the fourth even. Let the first hole be 1, the second hole be 2; the number of possible sets for the third and fourth hole is $N(m-1, 2m-2)$. Thus we get the following table:

1st hole:	2nd hole:	3, 4 hole:
1	2	$N(m-1, 2m-2)$
	4	$N(m-1, 2m-4)$
	\vdots	
	$2m-2$	$N(m-1, 2)$.

So

$$N_1(m-2, 2m) = \sum_{j=1}^{m-1} N(m-1, 2m-2j).$$

If the first hole is 3, then by same reasoning,

$$N_2(m-2, 2m) = \sum_{j=2}^{m-1} N(m-1, 2m-2j).$$

Thus

$$N(m-2, 2m) = \sum_{k=1}^{m-1} \sum_{j=k}^{m-1} N(m-1; 2m-2j).$$

Define $q = m - p$, and then set $n \equiv m - j$. We find that the above relations suggest

$$N(q, 2m) = \sum_{k=0}^{m-q} \sum_{n=q-1}^{m-k-1} N(q-1, 2n).$$

Expanding and setting $r \equiv m - k$ yields

$$N(q, 2m) = \sum_{r=1}^{m-q+1} r N(q-1, 2m-2r). \quad (\text{B1})$$

For $q=1, 2$, where we have calculated this relation, we find

$$N(q, 2m) = \binom{m+q}{2q}. \quad (\text{B2})$$

We then prove this relation for general q by induction. In terms of p ,

$$N(p, 2m) = \binom{2m-p}{2m-2p} = \binom{2m-p}{p}.$$

To find $N(p, 2m-1)$, use the obvious relation

$$N(p, 2m-1) = N(p, 2m) - N(p-1, 2m-2) = \binom{2m-1-p}{p}. \quad (\text{B3})$$

Equation (5) therefore becomes

$$y^{2m-1} + \sum_{p=1}^{m-1} y^{2m-1-2p} (-1)^p \left(\frac{U^2 F}{4\pi^2} \right)^p \binom{2m-1-p}{p} = 0, \quad (\text{B4})$$

or

$$\sum_{p=0}^m (-1)^p y^{2m-1-2p} \left(\frac{U^2 F}{4\pi^2} \right)^p \binom{2m-1-p}{p} = 0.$$

In terms of $q \equiv m - p$, we find

$$\sum_{q=0}^m (-1)^q \binom{m+q-1}{2q-1} Z^q = 0, \quad (\text{B5})$$

where

$$Z = \frac{4\pi^2 y^2}{U^2 F}. \quad (\text{B6})$$

Equation (B5) is equivalent to

$$\sum_{q=1}^m \frac{(\frac{1}{4}Z)^q}{(q-1)!} \frac{(m)_q (-m)_q}{(\frac{1}{2})_q} = 0, \quad (\text{B7})$$

where

$$(m)_q = \Gamma(m+q)/\Gamma(m).$$

Equation (B7) becomes

$$\sum_{q=0}^m \frac{(\frac{1}{4}Z)^q}{q!} \frac{(m+1)_q (-m+1)_q}{(\frac{3}{2})_q} = 0, \quad (\text{B8})$$

or, in terms of hypergeometric functions,

$$2F_1(m+1, -m+1, \frac{3}{2}, \frac{1}{4}Z) = 0, \quad (\text{B9})$$

which is equivalent to

$$\frac{\sin 2m\varphi}{\sin 2\varphi} = 0,$$

where $Z/4 = \sin^2 \varphi$. Hence

$$\varphi = r\pi/2m, \quad r = 1, 2, \dots, m-1.$$

The energy levels are therefore determined by

$$y^2 = (u^2 F / \pi^2) \sin^2(r\pi/2m).$$